Final Report for AOARD Grant "Graphene and Donor-Acceptor Molecules/Composites for Advanced Electronics Technologies"

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Abstract:

We have carried out a large number of studies using AOARD grant. We have acknowledged AOARD on all these publications related to the project, which is listed below. Here, we give abstract of all the works carried out under this grant.

We have used first-principles density functional theory (DFT) calculations for a systematic study on the structural stability, electronic, magnetic and transport properties of zigzag BNC nanoribbons (ZBNCNRs) consisting of boron–nitrogen (B–N) separated polyacene chains across the ribbon width. Studies have also been done to note the changes in structures and electronic properties of two-dimensional single-layer graphene in the presence of non-covalent interactions induced by carbon and boron fullerenes (C_{60}, C_{70}, C_{80} and B_{80}) and spin-polarized first-principles calculations performed on zigzag boron−nitride nanoribbons (z-BNNRs) with lines of alternating fused pentagon and heptagon rings (pentagon−heptagon line defect) at a single edge as well as at both edges [Ref 1, 2 5].

Studies have been done focusing on hydrogenation mechanism of CO_2 on Ni(110) surface catalyst using DFT study [Ref: 3]. DFT calculations have also been carried out to shed light on the electronic structure, optical properties and hydrogen adsorption capability of neutral MB_9 (where M = Li_3, Na_3, K_3, Al, Ga, In, Rh and Co) clusters [Ref: 4]. In another work we have investigated the energetics, electronic structure, optical properties, and charge transfer characteristics of coronene and its imide-functionalized derivatives using quantum chemical calculations [Ref: 6].

Atomistic molecular dynamics (MD) have been done to investigate the structure and energetics of single-stranded(ss)DNA assisted solubilisation of single-layer graphene in aqueous medium at room temperature, using ssA_{12}, ssG_{12}, ssC_{12} and ssT_{12} [Ref: 7] as well as to understand the binding mechanism of various chiral single-walled carbon nanotubes (SWCNTs) and single-stranded DNA (ssDNA) of four different nucleobase sequences (i.e., $ssdA_{14}$, $ssdT_{14}$, $ssdG_{14}$, and $ssdC_{14}$, where, A, T, G, and C are adenine, thymine, guanine, and cytosine, respectively) in aqueous media at room temperature (300 K) and atmospheric pressure (1 atm) [Ref: 8]. Also using DFT calculations work have been carried out to understand the structural, electronic, optical and energetics of duplex DNA containing metal-mediated base pairs [Ref: 9].

In the transport property front, we have dealt with structural distortion of $Fe(benzene)_2$

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14. ABSTRACT

14. ABSTRACT This report summarizes research findings from computational studies across multiple topic areas, including 1) electronic, optical, and charge transport in boron nitride (BN) nanoribbons and functionalized coronenes; 2) adsorption properties of carbon/boron fullerenes with graphene and hydrogen with B9/metal-B9 clusters; 3) binding of single-stranded ss-DNA with graphene and with single-walled carbon nanotubes (SWCNT); and 4) methane formation from hydrogenation of carbon dioxide (CO2). The research used first-principles density functional theory (DFT) calculations to perform a systematic study on the structural stability, electronic, magnetic and transport properties of zigzag BNC nanoribbons (ZBNCNRs) consisting of boron?nitrogen separated polyacene chains across the ribbon width. Studies were also done to note the changes in structures and electronic properties of two-dimensional single-layer graphene in the presence of non-covalent interactions induced by carbon and boron fullerenes (C60, C70, C80 and B80). Spin-polarized first-principles calculations were performed on zigzag boron−nitride nanoribbons (z-BNNRs) with lines of alternating fused pentagon and heptagon rings (pentagon−heptagon line defect) at a single edge as well as at both edges. Transport properties studies also dealt with structural distortion of Fe(benzene)2 and Fe2(naphthalene)2 considering their different spin states; electronic properties analyzed from band structure calculations and the transport characteristic of finite size Fe3-bis(3-BNacene), where it has been coupled to gold electrodes were also investigated. Other studies examined the energetics, electronic structure, optical properties, and charge transfer characteristics of coronene and its imide-functionalized derivatives using quantum chemical calculations. DFT calculations have also been carried out to shed light on the electronic structure, optical properties and hydrogen adsorption capability of neutral MB9 (where M = Li3, Na3, K3, Al, Ga, In, Rh and Co) clusters and on the mechanism of hydrogenation of CO2 on a Ni(110) surfaces. Atomistic molecular dynamics (MD) were done to investigate the structure and energetics of ss-DNA assisted solubilization of single-layer graphene in aqueous medium at room temperature, using ssA12, ssG12, ssC12 and ssT12 as well as to understand the binding mechanism of various chiral single-walled carbon nanotubes (SWCNTs) and single-stranded DNA (ssDNA) of four different nucleobase sequences (i.e., ssdA14, ssdT14, ssdG14, and ssdC14, where, A, T, G, and C are adenine, thymine, guanine, and cytosine, respectively). DFT calculations were also carried out to understand the structural, electronic, optical and energetics of duplex DNA containing metal-mediated base pairs.

15. SUBJECT TERMS

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and Fe_2(naphthalene)$_2$ considering their different spin states; electronic properties analyzed from band structure calculations and the transport characteristic of finite size Fe_3-bis(3-BNacene), where it has been coupled to gold electrodes on either side has been investigated [Ref:10].

Results and Discussions:

Graphene and graphene nanoribbons have attracted huge attention in the recent years and we have also focused our attention to a certain extent on working in this field. Effect of edge states on the electronic, magnetic and transport phenomenon has been studied for BN-fused polyacene nanoribbons with zigzag edges, wherein using DFT calculations we have tried to take an insight into the effect of edges and varying widths on the abovementioned properties. Herein we find that all of the ZBNCNRs considered here show moderate cohesive energy and favorable formation energy with the lower value obtained for the $C_{pass}C_{pass}$ ZBNCNR (pass=passivated, Z=zigzag, BNCNR= BNC nanoribbon) indicating its preferred thermodynamic stability among all. For all of the considered ribbon widths (nanoribbons with 6, 8, 10, and 12 zigzag chains), we find that all ZBNCNRs with either bare B and N atoms at both edges or bare B and N at opposite edges show metallic behavior, while the one with hydrogen passivated B and N at opposite edges exhibits semiconducting properties regardless of the ribbon widths. Also ZBNCNRs with hydrogen passivated C at the B–N chain edges display a range of conduction types, including half-metallic and metallic behavior depending on the ribbon widths. The smaller width ribbons (6 and 8 zigzag chains) show half-metallic behavior, whereas for the larger ribbon widths (10 and 12 zigzag chains), we find a metallic state [Ref:1]. In another work [Ref: 5], we have also looked into the origin of magnetic and electronic properties of BN nanoribbons, instead of the earlier BNC nanoribbons, with even and odd-line Stone-Wales' defect or a 5-7 defect, where we find that among the different spin-configurations that we have studied, the spin-configuration with ferromagnetic ordering at each edge and antiferromagnetic ordering across the edges is quite interesting. For this spin configuration, we find that, if the introduced pentagon-heptagon line defect is odd-numbered, the systems behave as spin-polarized semiconductors, but, for even-numbered, all the systems show interesting antiferromagnetic half-metallic behavior; the reasons for such properties has also been traced back to the nature of edge states.

Two-dimensional single layer graphene has been further utilized in its study of structural and electronic property changes in presence of carbon and boron fullerenes. Our study shows that larger carbon fullerene interacts more strongly than the smaller fullerene, and boron fullerene interacts more strongly than that of its carbon analogue with the same nuclearity. We find that van der Waals interactions play a major role in governing non-covalent interactions between the adsorbed fullerenes and graphene. Moreover, a greater extent of van der Waals interactions found for the larger fullerenes, C_{80} and B_{80}, relative to smaller C_{60}, and consequently, results in higher stabilisation. We find a small amount of electron transfer from graphene to fullerene, which gives rise to a hole-doped material [Ref: 2].

Studies on interaction of DNA with graphene [Ref: 7] and single walled carbon nanotubes (SWCNT) [Ref: 8] have been done using Molecular Dynamics simulation. For SWCNT we found from simulations studies that single-stranded (ss) DNA undergoes rapid structural changes and wrap around the SWCNTs via π-stacking interactions between SWCNT's wall and the nucleobases of ssDNA. Our computations demonstrate that the length of the ssDNA plays an important role during the wrapping process. In order to understand the electronic contributions of these systems, the quantum calculations have been performed at Hartree−Fock level for the 17 ns MD simulated structures. The quantum chemical calculations provide evidence that the highly stable ssDNA@SWCNT hybrid possesses a larger HOMO−LUMO gap.

For DNA and graphene, we chose four different ssDNA of homologous base sequence, $ssdA_{12}$, $ssdG_{12}$, $ssdC_{12}$, $ssdT_{12}$ (A = Adenine, G = Guanine, C = Cytosine and T = Thymine), and we find that there exist simultaneously two major competing forces: nucleobase–nucleobase intra-molecular p–p stacking interactions and nucleobase–graphene inter-molecular p–p stacking interactions. The former interactions help to maintain ssDNA helical geometry, whereas the latter interactions assist the ssDNA with becoming surface adsorbed on graphene. Note that both types of interactions strongly depend on the chemical nature of nucleobase and the sequence type present in various ssDNA. The calculated binding free energy strength between various ssDNA and graphene follows the order of: ssd(AGTC)3 > ssdA12 > ssdG12 > ssdC12 > ssdT12. The trend in binding free energy has been rationalized in terms of the adsorption strength of individual nucleoside over graphene, number of base–graphene p-stacks, together with the nature of nucleobase (purine: A, G and pyrimidine: C, T) present in different ssDNA sequences. Focus has also been on structural, energetic, electronic, and optical properties of synthesized duplex DNA containing metal-mediated base pairs. The studied duplex DNA consists of three imidazole (Im) units linked through metal (Im-M-Im, M=metal) and four flanking A:T base pairs (two on each side). Here we examined the role of artificial base pairing in the presence of two distinctive metal ions, diamagnetic Ag^{+} and magnetic Cu^{2+} ions, on the stability of duplex DNA and we found that metal-mediated base pairs form stable duplex DNA by direct metal io coordination to the Im bases. Our results suggest a higher binding stability of base pairing mediated by Cu^{2+} ions than by Ag^{+} ions, which is attributed to a larger extent of orbital hybridization [Ref: 9].

Studies have also been carried out on complete hydrogenation mechanisms of CO_2 on Ni(110) surface catalyst using density functional theory. Here we studied the possible hydrogenation mechanism to form methane from the stable adsorption–co-adsorption intermediates of CO2 and H2 on Ni(110) surface. Our computations clearly elucidate that the mechanism for the formation of methyl, methoxy and methane moieties from carbon dioxide on the nickel catalyst and also show that the methane formation via hydroxyl carbonyl intermediate requires a lower energy barrier than via carbon monoxide and formate intermediates on the Ni(110) surface [Ref: 3]. Density functional theory has also been used for shed light on the electronic structure, optical properties and hydrogen adsorption capability of neutral MB_9 (where M = Li_3, Na_3, K_3, Al, Ga, In, Rh and Co) clusters. Electronic structural studies on the parent B_9^{3-} clusters reveal that less aromatic hypervalent B-centered B_8 ring geometry is energetically more favored. However, GM^{3+} (Al, Ga and In) in GM@B_9 prefers a highly aromatic metal-centred 9-membered molecular wheel structure. In addition, the larger size of indium breaks the D_{9h} symmetry of the molecular wheel by coming slightly out of the ring plane unlike Al@B_9 and Ga@B_9. Metal@B_9 molecular wheels show optical absorption in a broad range of the spectrum (from UV to NIR: 260–1000 nm), which is attributed to the metal's ability to perturb the ring centered excited state [Ref: 4].

Coronene being a small hexagonal nanoflake of graphene, we have also studied the structural, opto-electronic and charge transfer properties of coronene and it's various imide-functionalized derivatives [Ref: 6]. Introduction of an imide group (imide is an electron-withdrawing group) into a pristine coronene moiety results in bathochromic shift in wavelength and these molecules find application in the optoelectronic industry. Also we have studied charge transfer properties of these systems using Marcus theory to get an idea of the nature of charge carrier transport in these systems. Coronene is predominantly a hole transporter according to our calculations. Moving to charge transport studies, we have worked on investigating the structural distortion of Fe(benzene)$_2$ and Fe_2(naphthalene)$_2$ considering their different spin states. It turns out from crystal-field splitting and 18-electron rule that the structure

is less distorted and more stable in its high-spin state than the corresponding low-spin state. A possible way to make the proper stacking of these Fe-based sandwiched complexes by packing one infinite chain of Fe between two polyacene and BNpolyacene ligands. We also have studied the structural, electronic, and magnetic properties of infinitely extended system, that is, Fe_{∞}-bis(polyacene) and BN-analogue of it Fe_{∞}-bis(BNpolyacene). The band structure calculations show that the electronic structures of these two systems are quite dissimilar; that is, Fe_{∞}-bis(polyacene) shows metallic behavior whereas its BNanalogue shows robust half-metallic behavior. We have also studied the transport characteristic of finite size Fe_3-bis(3- BNacene) where it has been coupled to gold electrodes on either side. From the transport calculations, we predict that under finite bias, Fe_3-bis(3-BNacene) shows efficient spin filter behavior, which possibly can have a huge application in spintronic devices [Ref: 10].

List of Publications and Significant Collaborations that resulted from your AOARD supported project: In standard format showing

a) Papers published in peer-reviewed journals:

1. Arun K. Manna and Swapan K Pati, "Effect of Edge States on the Electronic, Magnetic and Transport Properties of BN-Fused Polyacene Zigzag Nanoribbons", *J. Mater. Chem. C*, **1**, 3439-3447 (2013)
2. Arun K. Manna and Swapan K Pati, "Computational Studies on Non-covalent Interactions of Carbon and Boron Fullerenes with Graphene", *ChemPhysChem*, **14**, 1844-1852 (2013).
3. Pallavi Bothra, Ganga Periyasamy, Swapan K. Pati, "Methane formation from the hydrogenation of Carbon dioxide on Ni (110) surface - A Density Functional Theoretical Study", *Phys. Chem. Chem. Phys.*, **15**, 5701 - 5706 (2013).
4. Swastika Banerjee, Ganga Periyasamy and Swapan K. Pati, Structural, optical and hydrogen adsorption properties of B9/metal-B9 clusters: A Density Functional Theoretical Study, *Phys. Chem. Chem. Phys.*, **15**, 8303 - 8310 (2013).
5. SRKC Sharma Yamijala and Swapan K Pati, "Electronic and Magnetic Properties of Zigzag Boron-Nitride Nanoribbons with Even and Odd-line Stone-Wales (5-7 pair) Defects", *J. Phys. Chem. C*, **117**, 3580 - 3594 (2013).
6. Somananda Sanyal, Arun K. Manna, Swapan K. Pati, "Effect of Imide Functionalization on the Electronic, Optical and Charge Transport Properties of Coronene: A Theoretical Study", *J. Phys. Chem. C*, **117**, 825 - 836 (2013).
7. Arun K. Manna and Swapan K. Pati, "Theoretical understanding of single-stranded DNA assisted dispersion of graphene", *J. Mater. Chem. B*, **1**, 091 - 100 (2013).
8. Siamkhanthang Neihsial, Ganga Periyasamy, Pralok K. Samanta and Swapan K. Pati, "Understanding the Binding Mechanism of Various Chiral SWCNTs and ssDNA: A Computational Study", *J. Phys. Chem. B*, **116**, 14754 - 14759 (2012).
9. Pralok K Samanta, Arun K Manna and Swapan K Pati, "Structural, Electrical and Optical Properties of Metallo Base-Pairs in Duplex DNA: A Theoretical Insight", *Chem. Asian J.*, **7**, 2718 - 2728 (2012).
10. Dibyajyoti Ghosh, Prakash Parida and Swapan Pati, "Electronic, Magnetic and Transport Properties of Fe_n-bis(n-acene) and Fe_n-bis(n-BNacene)[$n=1,2,\infty$]: A Theoretical Study", *J. Phys. Chem. C*, **116**, 18487 - 18494 (2012).

c) Conference presentations: None

d) Manuscripts submitted but not yet published:

1. Pralok K. Samanta and Swapan K. Pati, "Structural, Electronic and Photophysical Properties of Analogues RNA Nucleosides: A Theoretical Study", 2013 (submitted).
2. Pralok K. Samanta and Swapan K. Pati, "Structural and Magnetic Properties of a Variety of Transition Metal Incorporated DNA Double Helices", 2013 (submitted).

e) Provide a list any interactions with industry or with Air Force Research Laboratory scientists or significant collaborations that resulted from this work.

We have interacted with Dr. Ruth Pachter of WPAFB and Dr. Rajesh Naik of AFMC (Dayton, Ohio). In fact, Dr. Naik and his group had already done one experimental works, where they could separate out carbon nanotubes using some DNA sequences, and they did not know the sequences of the DNA structure that they had used. We have done extensive theory to find the DNA sequences and the corresponding separation of carbon nanotube structures with various chiralities (see Ref [8] above). However, none from Dayton scientists have been co-authored. I would like to interact again, if I get a chance in future. It would be nice to work with experimentalists, giving them complete theoretical microscopic understanding of their experimental outputs.

DD882: As a separate document, please complete and sign the inventions disclosure form.

We have completed and signed the DD882 form and attached please find the scanned pdf file of DD882 with signature (Thanks also to Dr. Kenneth Caster for help in filling up several parts of the DD882 form).